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Catalytic Activation of Unstrained, Nonactivated Ketones Mediated by Platinum(II): Multiple C−C Bond Cleavage and CO Extrusion
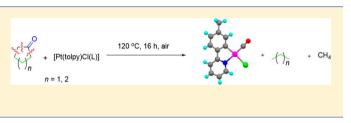
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S *Supporting Information*

ABSTRACT: The complexes $[Pt(tolpy)Cl(L)]$ (tolpy = 2-(4-tolyl)pyridyl; L = dmso, dms, py, PPh$_3$, CO) are precursors for the catalytic cleavage of C−C bonds and extrusion of CO from a series of unactivated ketones such as cyclohexanone; deuterium labeling experiments demonstrate the involvement of a transfer hydrogen step in the mechanism.
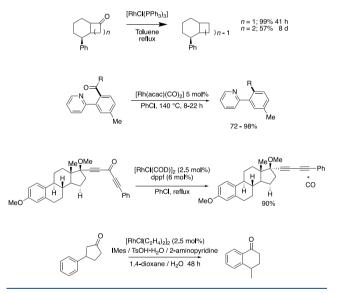
Catalytic decarbonylation reactions have the potential to be synthetically useful, atom-economical transformations for a commonly encountered functional group, potentially affording compounds that might otherwise be difficult to access.[1−6] Such reactions are well-known and trivial with aldehydes, but ketones present a significantly greater challenge.[1] For example, Gozin et al. and Ameen et al. highlighted the importance of transition-metal-catalyzed C−C bond cleavage in petroleum refinement and the processing of oxygen-rich bioderived fuels.[7,8]

Stoichiometric extrusion of a carbonyl fragment was first reported in 1965 by Rusina and Vlcek when cyclohexanone was heated with RhCl$_3$ and PPh$_3$, affording $[RhCl(CO)(PPh_3)_2]$ and unknown hydrocarbon products.[9] Since then, most examples of ketone decarbonylation have employed strained substrates[10−13] or those that allow tethering of the substrate to the metal via a directing group (e.g., Scheme 1—arylpyridine example).[14−19] These reactions, which are normally stoichiometric, are often mediated by coordinatively unsaturated rhodium complexes,[20,21] with forcing conditions, high temperatures, and long reaction times being required.[22−24] However, in 2016 Lee et al. achieved ketone C$_\alpha$−C$_{CO}$ bond activation of a number of systems, including cyclohexanone, at room temperature using a rhodium(II) porphyrin system generating Rh(II)-acyl complexes. While this approach does not lead to decarbonylation, the mild reaction conditions reflect a significant improvement on the earlier results.[25] More recently, Dong and co-workers have developed an elegant catalytic strategy for C$_\alpha$−C$_{CO}$ bond activation in which the carbonyl is activated by catalytic amounts of amine or carbene and the thermodynamic driving force is provided by concomitant formation of new C−C bonds.[26]
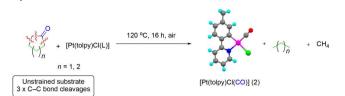
As part of earlier studies on ortho-platinated 2,5-bis(4-alkoxyphenyl)pyridines,[27] Pt^{III} dimers were formed unexpectedly via oxidation of the Pt^{II} complexes by free or bound dmso in the presence of acid, consistent with related oxidations reported previously by Kukushkin et al.[28,29] and Alexandrova et al.[30,31] In further studies of this reaction, the surprising observation was

Scheme 1. Examples of Metal-Mediated C−C Activation of Ketonic Substrates with Strained[10] or Tethered[4,16,26] Substrates

made that heating $[Pt(tolpy)(Cl)(S\text{-}dmso)]$ (**1**; tolpy = 2-(4-tolyl)pyridyl) in air with cyclohexanone afforded the known[32] complex $[Pt(tolpy)(Cl)(CO)]$ (**2**; Scheme 2), characterized by ν_{CO} 2098 cm^{-1}, $\delta(^{195}Pt)$ −3947 ppm and by single-crystal X-ray methods (see the Supporting Information for details). With **1** and cyclohexanone as the only reagents, the carbonyl ligand evidently came from decarbonylation of cyclohexanone with accompanying C−C bond cleavage. To the best of our knowledge, this transformation has remained undeveloped since the report of cyclohexanone decarbonylation by Rusina and Vlcek.[9] More than 50 years on from their report, our

Scheme 2. Platinum-Catalyzed Activation of Cyclohexanone[a]

[a]The transformation involves the cleavage of the three C−C bonds indicated. The X-ray single crystal structure of **2** is illustrated.

observation provides an opportunity to study this transformation in greater detail.

Thus, GC and GC-MS analysis of the headspace gas after reaction of cyclohexanone with **1** confirmed the formation of butane and methane, with trace amounts of other small hydrocarbons (see Scheme 2), as detailed in the Supporting Information. In fact, the reaction of cyclopentanone with **1** under the same conditions showed the formation of methane and propane, thereby suggesting that both substrates are activated via the same mechanism. Rusina and Vlcek[9] did not report an analysis of any organic products, and so their reaction was repeated, revealing the formation of butane, cyclohexane, cyclohexene, and benzene in the approximate ratio of 1:0.8:1:3, implying a different mechanistic route in their case.

Given the known photochemical instability of cyclohexanone and cyclopentanone in the gas phase,[33] and reports of photochemical C−C bond activations,[34] control experiments established that activation of cyclohexanone mediated by **1** proceeded in the absence of natural light to give the same products. In addition, irradiation of a room-temperature solution of **1** in cyclohexanone (λ_{max} 254 nm) at room temperature led to no observable reaction, confirming that the decarbonylation is thermal in nature.

To investigate the reaction further, it was carried out in the presence of the related complexes **2−6** (Figure 1) which, like **1**, have a neutral fourth ligand. Complex **6** was found to be inactive, while **2−5** led to reactions, and important in these observations is that **2** is active, showing that the process is catalytic. The related dimer **7** was also active. The Pt complexes **8−10**, each
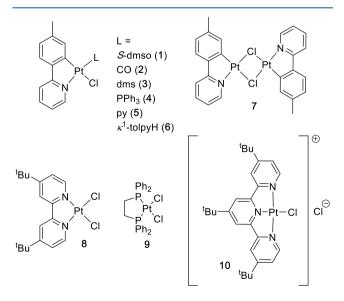

Figure 1. Complexes tested for the thermal decarbonylation of ketones.

with a neutral chelating ligand, were also evaluated and neither **9** nor **10** showed any evidence of decarbonylation. Complex **8** did, however, show the formation of butane and the starting complex was the only one that could be identified at the end of the reaction. Palladium analogues of **1** and **7** were not active, suffering extensive decomposition even at low reaction temperatures.

Returning to the organic products, the reaction stoichiometry shows a significant imbalance in hydrogen content to the extent of four hydrogen atoms:

$$C_6H_{10}O \text{ (cyclohexanone)}$$
$$\rightarrow C_4H_{10} + CH_4 + CO \ (\equiv C_6H_{14}O)$$

With no other reagents present, this hydrogen must arise from the cyclohexanone substrate, suggesting the possibility of a transfer hydrogenation process. While cyclohexanone is not generally known for its utility in such chemistry, Izawa et al. did show some precedent for such a reaction, reporting a palladium-mediated oxidation/aromatization of cyclohexanone to phenol.[35]

Therefore, to demonstrate a transfer hydrogenation step, the reaction of cyclohexanone with complex **1** was repeated in the presence of 1,3-cyclohexadiene, which is well-known as a transfer hydrogenation donor.[36] At the end of the reaction, benzene (formed when cyclohexadiene acts as a transfer hydrogenation substrate) was observed as a product by electronic spectroscopy, strongly supporting the involvement of transfer hydrogenation.

Further compelling evidence for the mediation of transfer hydrogenation comes from the observation that, while acetone does not react thermally with complex **1**, when the reaction is carried out in the presence of 1,3-cyclohexadiene, formation of **2** along with methane and CO is observed. Likewise it is found that acetophenone will only react in the presence of the transfer hydrogenation substrate. Furthermore, carrying out the reaction with acetone-d_6 led to the formation of CD_3H, confirming that 1,3-cyclohexadiene is the source of the hydrogen atoms incorporated in the product. This observation is significant, as there is only a single previous report of the decarbonylation of acetone.[37]
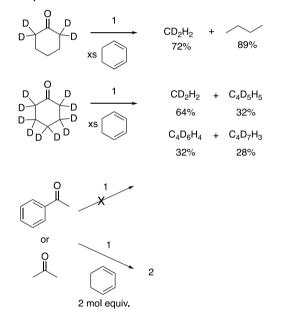
An important observation, however, is that the activation of these ketones by complex **1** is accompanied by the formation of particulate Pt with average hydrodynamic radius 10−50 nm, as determined by dynamic light scattering. Addition of mercury to the reaction mixture[38] led to a significant reduction in the formation of butane, suggesting intervention by these platinum nanoparticles. However, when the reaction is tracked by in situ infrared spectroscopy, immediate formation of complex **2** is observed, which would suggest that an early decarbonylation step is homogeneous (a heterogeneous process would typically require an induction period as the nanoparticles form). In addition, it is observed that, when cyclohexanone is heated with either **6** or **10**, nanoparticles are formed but there is no decarbonylation. This would also support the proposal of an early, homogeneous decarbonylation step. Transfer hydrogenation, however, may be mediated by the platinum nanoparticles.

Previous examples of C−C bond scission with coupled decarbonylation (e.g., Scheme 1) have typically led to simple extrusion of CO, and while no mechanistic detail was given, the fact that the present reaction with cyclohexanone give a different range of products would imply a different mechanism. Thus, it is

assumed that the ketone coordinates to Pt (either η^1 through oxygen or η^2 through C=O) following dissociation of the neutral, monodentate ligand (L in Scheme 2), after which the C–C bond α to the carbonyl is cleaved (analogy with the formation of metal-acyl complexes in the Rh[II]-porphyrin systems).[25] A second C–C cleavage β to C=O would then extrude an oxygenated C_2 unit (which would readily fragment to CO and methane) leaving a C_4 moiety.

Support for these suggestions comes from deuterium cross-labeling studies conducted using cyclohexanone-d_{10} with 1,3-cyclohexadiene as the transfer hydrogen donor. Under these conditions, the major C_1 product was CD_2H_2 (64%), which suggests a fairly selective reaction (consistent with a homogeneous process), while butane was found as a mixture of isotopomers, mainly $C_4D_5H_5$ (32%), $C_4D_6H_4$ (32%), and $C_4D_7H_3$ (28%), more consistent with a relatively unselective heterogeneous process. Similarly, use of 2,2,6,6-tetradeuteriocyclohexanone and 1,3-cyclohexadiene gave 72% CD_2H_2 (again quite selective) and 89% C_4H_{10}. Some of the key mechanistic observations are collected in Scheme 3.

Scheme 3. Complexes Tested for the Thermal Decarbonylation of Ketones[a]

[a]The percent refers to the proportion of that isotopomer as a proportion of all isotopomers of that compound.

In summary, we have achieved the cleavage of C–C bonds in unstrained and nonactivated ketones such as cyclopentanone and cyclohexanone through the action of $[Pt(tolpy)(Cl)(L)]$ (1–5) in a thermal process. Decarbonylation occurs alongside a transfer hydrogenation step, where evidence suggests mediation by platinum nanoparticles. Suppression of nanoparticle activity or formation does not prevent decarbonylation, leading to the conclusion that this process is homogeneous, a proposal supported by cross-labeling studies.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00650.

Details of complex synthesis and of the different reactions (PDF)

Accession Codes

CCDC 1956985 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

The manuscript was written through contributions of all authors.

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